

WPI659712 05 DEC 2005

1 METHOD

2

3 This invention relates to a method of insulating
4 submerged structures, particularly but not
5 exclusively conduits adapted to transfer fluids from
6 subsea hydrocarbon reservoirs to a service platform.

7

8 A plurality of conduits or pipes of relatively small
9 diameter typically extend from a seabed structure to
10 a service platform and are enclosed within an outer
11 'carrier' pipe. Such an arrangement is known as a
12 'pipeline bundle', and is adapted to convey produced
13 fluids from the well.

14

15 Additionally, having flowed along the pipelines or
16 bundles, hydrocarbons are then transported to the
17 surface for processing via vertical structures which
18 can be either single pipes or a plurality of pipes.
19 Such an arrangement is known as a 'riser' and is
20 adapted to convey fluids from the seabed to the
21 surface for processing and treatment.

22

1 When fluids are extracted from subsea reservoirs,
2 their temperature is normally higher than that of
3 the surrounding water. As the fluids cool in the
4 pipes to the temperature of the water, certain
5 compounds come out of solution, and this causes
6 problems with precipitates such as waxes or gas
7 hydrates that build up within the pipelines and can
8 reduce or prevent the flow of hydrocarbons.
9 Moreover, the viscosity of the produced fluids
10 increases as their temperature decreases, which also
11 reduces the rate of flow through the pipeline.
12 Additionally if gas comes out of solution it can,
13 under certain conditions of pressure and
14 temperature, combine with water to form clathrate
15 structures known as 'Hydrates' which can accumulate
16 within the pipeline causing blockages reducing or
17 preventing the flow of hydrocarbons.
18
19 It is known to insulate pipeline bundles in several
20 ways to offset these problems - for instance pipes
21 are often insulated using solid syntactic foam
22 preformed insulating coatings. Alternatively the
23 pipe-in-pipe annular spaces are evacuated, or are
24 filled with silica-based materials or hollow spheres
25 of plastic material in a synthetic resin matrix.
26
27 These and similar techniques have serious
28 disadvantages in the way of investment cost,
29 difficulty of handling, and the requirement for
30 specialist equipment to manufacture the materials,
31 and as a consequence the materials needed for the
32 techniques are not routinely made up at the point of

1 manufacture of the pipeline. Also some of the
2 materials needed for the insulation are limited with
3 respect to the depth of water in which they can be
4 applied. For example, at depths beyond around 1500
5 metres the hydrostatic pressure of the water column
6 will collapse foam and its insulating qualities will
7 be lost.

8

9 A further attempt to solve this problem is disclosed
10 in European Patent Publication N° 0,336,493. In
11 this application, a liquid hydrocarbon gel is
12 provided in the outer pipe to insulate the smaller
13 diameter pipes running therethrough. However, the
14 use of a fluid gel requires the provision of a
15 pressure balancing system which is prone to failure.

16

17 Other subsea structures, such as trees provided at a
18 wellhead, can also require insulation.

19

20 According to the present invention, there is
21 provided a method of insulating a subsea structure,
22 the method comprising:

23 injecting a substance into the subsea structure;
24 allowing said substance to form a gel, wherein
25 the formed gel has a dynamic viscosity of more
26 than 1000Pa.S.

27

28 Preferably the subsea structure comprises a first
29 conduit, more preferably said first conduit
30 enclosing a second conduit.

31

1 Preferably, the conduits are tubulars, such as
2 oilfield tubulars.

3

4 Preferably, the substance is injected into an
5 annular space between the first and second conduits.

6

7 Preferably the thermal properties of the gel can be
8 varied over the length of a conduit or series of
9 conduits. The thermal properties can include
10 density, specific heat capacity, and conductivity of
11 the gel.

12

13 Preferably, the gel can retain its integrity
14 unsupported.

15

16 In this context, 'retain its integrity unsupported'
17 means a gel that can, for example, be sliced into
18 pieces and can maintain its form when dropped from a
19 height, but cannot be poured or pumped.

20

21 Preferably, the substance is a pourable fluid prior
22 to gellation.

23

24 Dynamic viscosities of gelled materials discussed in
25 this patent are considerably in excess of 1000 Pa.S,
26 preferably 2000 Pa.S to essentially solid materials
27 which do not flow and thus have a viscosity of over
28 5,000,000 Pa.S.

29

30 Preferably, the substance comprises a fluid which
31 has a comparatively high specific heat capacity and

1 a second fluid which has a comparatively low thermal
2 conductivity.

3

4 More preferably, the first fluid is water and the
5 second fluid is a hydrophobic fluid such as a
6 hydrocarbon-containing fluid or a vegetable oil.

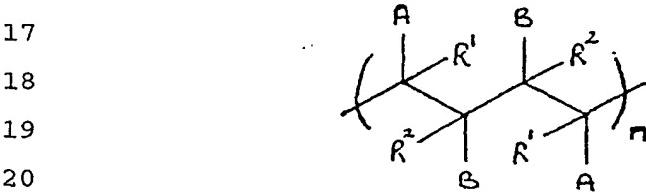
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8 The relative proportions of the first and second
9 fluids can be adjusted depending on the nature of
10 the hydrocarbons being recovered, the specific
11 pipeline arrangement and the subsea environment.

12

13 Preferably, the substance further comprises a first
14 and second polymeric compound. The first polymeric
15 material may have a general formula

16



22 wherein A and B are the same or different wherein at
23 least one comprises a relatively polar atom or group
24 and R¹ and R² independently comprise relatively non-
25 polar atoms or groups.

26

27 Preferably, R¹ and R² are hydrogen atoms although
28 they may be other relatively non-polar atoms or
29 groups, for example, alkyl groups.

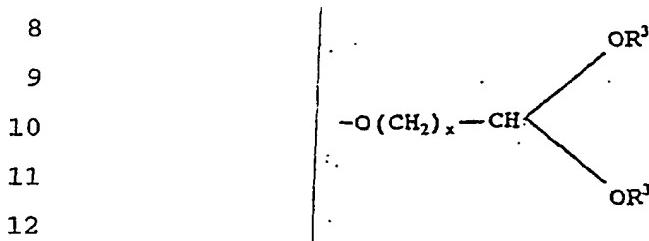
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31 Preferably, A and B are independently selected from
32 optionally-substituted alkyl, cycloalkyl,

1 cycloalkenyl, cycloalkynyl, aromatic and
2 heteroaromatic groups.

3

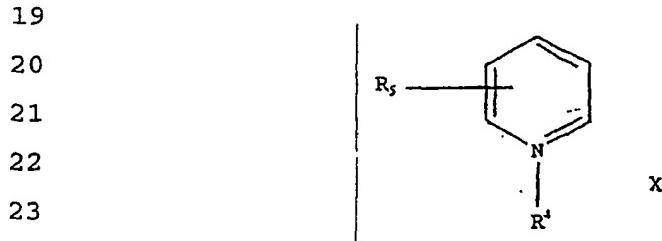
4 More preferably, A represents a phenyl group
5 substituted, preferably at the 4-position relative
6 to the group C-C, by a formyl group or a group of
7 general formula:



13 wherein x is an integer from 1 to 6 and each R³ is
14 independently an alkyl or phenyl group or together
15 form an alkene group.

16

17 More preferably, group B represents a group of
18 general formula:



25 wherein R⁴ represents a hydrogen atom or an alkyl or
26 aralkyl group, R⁵ represents a hydrogen atom or an
27 alkyl group and X⁻ represents a strongly acidic ion.

28

29 Other options for the groups A, B and R¹ - R⁵ are
30 disclosed in British Patent Publication GB
31 2,317,895A the disclosure of which is incorporated
32 herein by reference.

1 Preferably, the second polymeric compound includes
2 one or more functional groups capable of reacting
3 with said first polymeric compound.

4

5 More preferably, the second polymeric compound
6 includes a functional group selected from an
7 alcohol, carboxylic acid, carboxylic acid
8 derivative, for example an ester, and an amine
9 group.

10

11 Even more preferably, the second polymeric compound
12 is selected from optionally substituted
13 polyvinylalcohol, polyvinylacetate, polyalkalene
14 glycols and collagen (and any component thereof).

15

16 Yet more preferably the second polymeric compound is
17 polyvinyl alcohol. Other possible second polymeric
18 compounds are disclosed in the aforementioned
19 British Patent Publication 2,317,895A.

20

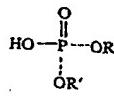
21 The substance may further comprise acid, such as
22 paratoluene sulphuric acid, to catalyse the reaction
23 between the first and the second polymeric
24 compounds.

25

26 In alternative embodiments, the substance may
27 comprise a third polymeric compound and a ferric
28 salt in addition to a hydrocarbon. Such alternative
29 embodiments preferably do not comprise the first and
30 second polymeric compounds nor water. Preferably
31 therefore, the alternative embodiments are effected
32 in a hydrocarbon phase.

1 Preferably, the third polymeric compound is a
2 phosphate, more preferably an orthophosphate, even
3 more preferably an orthophosphate ester.

4 Preferably, the orthophosphate esters have the
5 structure of formula:



9 wherein R is a straight or branched chain alkyl or
10 alkaryl group having about 6 to about 18 carbon
11 atoms and R' is hydrogen or an aryl, alkaryl or
12 alkyl group having about up to 18 carbon atoms.

13
14 Preferably, about 0.3% to 3 wt% by weight, based on
15 the hydrocarbon/water liquid, of the phosphate is
16 added.

17
18 Preferably, the ferric salt and third polymeric
19 compound are added in an equimolar ratio. More
20 preferably, the alternate embodiment forms a gel as
21 described in US Patent 5,417,287, the disclosure of
22 which is incorporated herein by reference.

23
24 Preferably, materials which undergo a change in
25 phase (such as going from liquid to solid) on
26 cooling are selected, as these release heat thereby
27 extending the time it takes for the tubular contents
28 to cool down.

29
30 Optionally, cenospheres may be added to the
31 substance in order to reduce thermal conductivity,
32 improve mechanical strength and lower density.

1 Optionally, spheres made of polymers and enclosing
2 hydrocarbon gas can be added to provide reduced
3 thermal conductivity and lower density.

4

5 Optionally waxes can be added to the hydrocarbon.

6

7 Preferably the waxes are highly branched chain
8 waxes.

9

10 Optionally some or all of the gelling components can
11 be incorporated within a wax of a known melting
12 point to either slow the rate of gel formation or
13 arrest it until the wax melts on the commencement of
14 production.

15

16 Optionally, antibacterial agents and/or corrosion
17 inhibitors can be added to the substance.

18

19 Optionally chemicals that scavenge free radical
20 materials can be added to the substance.

21

22 According to a second aspect of the present
23 invention, there is provided a method of insulating
24 a submerged conduit, the method comprising the steps
25 of:

26 applying at least one substance to the conduit
27 before it is submerged; then,

28 submerging the conduit under water; and

29 allowing the substance to form a gel.

30

31 Preferably the method employs the methods set out
32 above.

1 Preferably, the tubular comprises further tubulars
2 enclosed therein.

3

4 Optionally the external tubular is manufactured out
5 of thin wall steel or a plastic, for example high
6 density polyethylene, such that the hydrostatic
7 pressure occasioned from the depth of water in which
8 the pipeline is immersed is transferred from the
9 outer pipe to the inner pipe with the gel acting as
10 a pressure transfer medium.

11

12 Preferably, the substance is applied to an annulus
13 between the tubular and the said further tubulars
14 enclosed therein.

15

16 According to a further aspect of the invention there
17 is provided a method of altering the buoyancy of a
18 subsea structure, the method comprising,

19 injecting a substance into the subsea structure;
20 allowing said substance to form a gel, wherein the
21 formed gel has a dynamic viscosity of more than
22 1000Pa.S.

23

24 Preferably the buoyancy is altered by the addition
25 of microspheres in the substance which reduces the
26 density of the gel.

27

28

29 According to a further aspect of the invention there
30 is provided a method of insulating a structure, the
31 method comprising:

32 injecting a substance into the structure;

1 allowing said substance to form a gel.

2

3 Embodiments of the present invention will now be
4 described by way of example only with reference to
5 the accompanying figures, in which:

6

7 Fig. 1 is a graph showing the viscosity of a
8 gel as a function of the amount of gellant
9 added;

10 Fig. 2 is a calibration curve of a graph used
11 for determining the thermal properties of
12 certain embodiments of the present invention;
13 Fig. 3 is a graph showing the conductivity of
14 various embodiments of the present invention
15 as a function of microsphere content; and,
16 Fig. 4 is a graph showing the specific heat
17 capacity of a number of gels in accordance
18 with the present invention.

19

20 Examples 1-4, 7 use an "all-oil" system, and were
21 made up according to a method described in US patent
22 5,417,287 the disclosure of which is incorporated
23 herein by reference.

24

25 Example 1

26

27 2.0 ml of Clearwater HGA 70 (an orthophosphate
28 ester) was added (although between 0.3 and 3.0% by
29 weight is suitable) to a beaker containing 150 ml of
30 DF 1 base oil from Atofina Ltd. To this mixture
31 2.0ml of Clearwater HGA 55S (a ferric salt) was
32 added dropwise into the stirred solution. The fluid

1 was left to gel for a period of 24 hours. In
2 practice however a gel formed typically between 2-5
3 minutes from adding the ferric source.

4

5 Some of the properties of this gel are set out in
6 table 1.

7

8

9 Example 2

10

11 7.5g of glass microspheres were added stirred into a
12 container holding 150 ml of base oil DF 1 from
13 Atofina Ltd.

14

15 Microspheres (also called Cenospheres) are small
16 glass hollow spheres of between 20 - 150 microns
17 such as can be extracted from volcanic ash or the
18 ash from coal-fired power stations. The addition of
19 cenospheres reduces thermal conductivity and
20 improves mechanical strength of the resulting gel.
21 However they are not essential to the invention.

22

23 To this mixture 1.5ml Clearwater HGA 70 (an
24 orthophosphate ester) was added (although between
25 0.3 and 3.0% by weight is suitable). The mixture was
26 gelled by the addition of 1.5ml of Clearwater HGA
27 55S (a ferric salt). Alternatively ferric sulphate
28 may be added at between 0.25 to 2.0 moles per mole
29 of phosphate ester. The fluid was left to gel for a
30 period of 24 hours. In practice however a gel formed
31 typically between 2-5 minutes from adding the ferric
32 source.

1 Some of the properties of this gel are set out in
2 table 1.

3

4 Example 3

5

6 A third gelled fluid insulating system containing
7 450 ml of base oil DF1, 90 g of wax Astorwax
8 F07745/B, Clearwater HGA 55S 4.5ml and Clearwater
9 HGA 70 4.5ml was similarly made up, following the
10 method of example 1.

11

12 After a period of time, typically between one and
13 twenty four hours, the mixture sets as a solid
14 jelly-like material. When this gel was heated to 80C
15 the wax dissolved but the gel characteristics were
16 retained. On cooling wax was found to be fully
17 dispersed.

18

19 Some properties of this gel are also set out in
20 table 1, below.

21

22 Example 4

23

24 A fourth gelled fluid was made. 40 g of
25 microspheres (glass bubbles k 37 from 3M
26 Corporation) were placed in a beaker with 20 ml of
27 Atofina base oil DF1. 0.2 ml Clearwater HGA 70 was
28 stirred into the solution. Ten ml of Atofina base
29 oil DF1 containing 0.2 ml Clearwater HGA 55S was
30 then added dropwise into the solution.

31

1 Some properties of this gel are also set out in
2 table 1, below.

3

4 In general the relative proportions of components in
5 the gelled fluid insulating medium were determined
6 using considerations of cost, ease of shipping to
7 manufacturing location and desired performance
8 characteristics.

9

10 Of particular interest is a measure of the rate of
11 cool down known as diffusivity, this is described
12 as:

13

14 Diffusivity = Conductivity (W/mK) / [Specific heat
15 capacity (J/kg/K) x Density kg/m³]

16

17 The diffusivity measurements are given in table 1
18 below.

1

Gel	Quantities of Components				Conductivity ⁽³⁾ W/mK	Specific Heat ⁽²⁾ J/kgK	Density ⁽⁴⁾ kg/m ³	Diffusivity m ² /s × 10 ⁻⁸
	DF 1 Base Oil (ml) ⁽¹⁾	Wax g	Other ml	Microspheres g				
1	150	0	2.0ml C'HGA 70 (phosphate ester) 2.0ml C'HGA 55S (ferric salt)	0	0.131	2310	790	7.178
2	150 ⁽¹⁾	0	1.5ml C'HGA 70 (phosphate ester) 1.5ml C'HGA 55S (ferric salt)	7.5	0.1106	1980	728	7.673
3	450	90	4.5ml C'HGA 70 (phosphate ester) 4.5ml C'HGA 55S (ferric salt)	0	0.1469	2524	820	7.098
4	20	0	0.2ml C'HGA 70 (phosphate ester) 0.2ml C'HGA 55S (ferric salt)	40	0.0723	nd	470	nd

2

3

4 Table 15 Notes:

6 [1] paraffinic oil base oil DF1.

7 [2] determined by differential Calorimetry ASTM
8 method C351.9 [3] Conductivity was measured using a non steady
10 state probe ASTM method D 5930-01

11 [4} Determined by calculation

12

13 Abbreviations

14

15 C'HGA 70 - Clearwater HGA 70 (phosphate ester)

16 C'HGA 55S - Clearwater HGA 55S (ferric salt)

1 Further examples have been carried out to test the
2 effectiveness of such a gelled fluid insulating
3 system as an insulator for a pipeline bundle.

4

5 Example 5

6

7 British Patent publication GB 2,317,895A discloses a
8 substance and a method of forming a gel, the
9 disclosure of which is incorporated herein by
10 reference. Examples 5, 6 and 8 are based on the
11 chemistry disclosed in GB 2,317,895A.

12

13 45g of oil (for example sunflower or vegetable oil)
14 were placed in a container to which 35g of
15 cenospheres were added and the mixture was stirred
16 for five minutes until the cenospheres were fully
17 dispersed.

18

19 In a separate beaker a mixture of 18g of water and
20 2g of polyvinylalcohol (PVA) was made up and the
21 mixture of sunflower oil and cenospheres was poured
22 into this and mixed together to form an emulsion
23 mixture of oil, water, PVA and cenospheres.

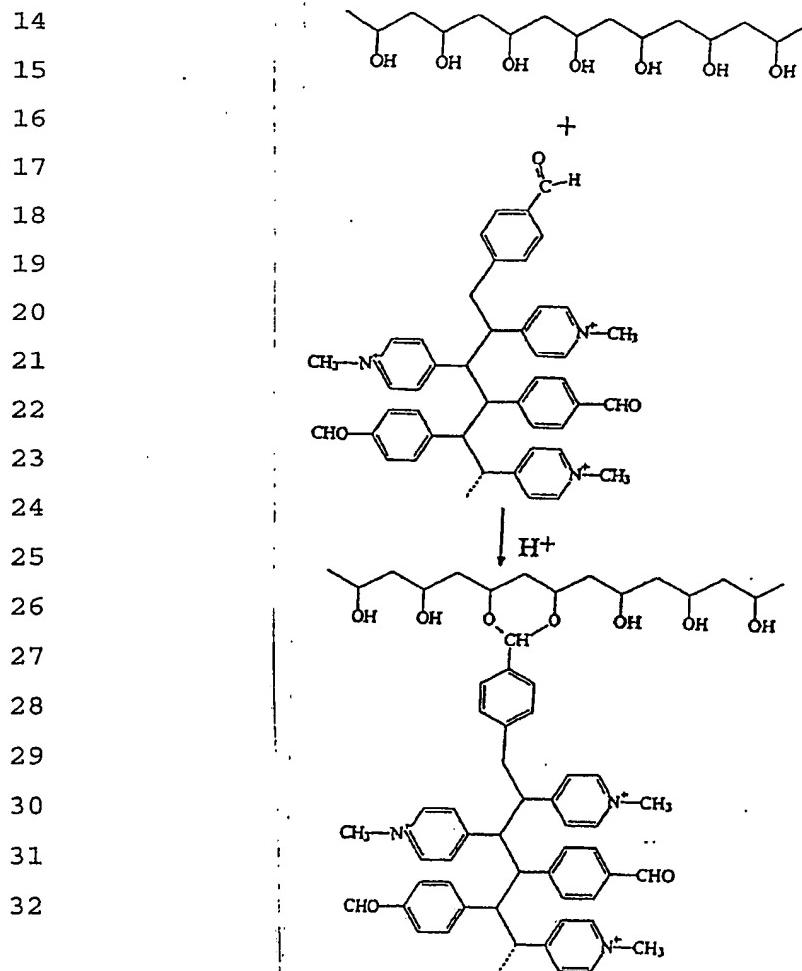
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25 An aqueous solution of 4-(4-formylphenylethenyl)-1-
26 methylpyridinium methosulphonate (SbQ) was added to
27 the mixture as a cross-linking agent. The resulting
28 mixture was then stirred and the contents of the
29 beaker were decanted into a 100ml measuring
30 cylinder. An acid was then added to catalyse the
31 change of phase of the mixture from liquid to gel.
32 An inorganic or organic acid may be used, examples

1 being hydrochloric acid, sulphuric acid, acetic
2 acid, and formic acid. The greater the quantity of
3 acid which is used, the quicker the rate of
4 formation of the gel. Thus the rate of formation of
5 the gel can be controlled by varying the amount of
6 acid used. The mixture was allowed to stand for a
7 period of twelve hours after which time a reaction
8 had occurred and a gel had formed.

9

10 An aldol condensation reaction between polymer
11 chains is effected to form the gel, that is a
12 reaction between the polyvinylalcohol and the SbQ
13 according to the reaction scheme below:



1 A determination of this material's thermal
2 conductivity was carried out using a Huskaflux non-
3 steady-state probe. The density was measured and the
4 specific heat capacity was calculated from existing
5 known values for each constituent in order to
6 determine the thermal diffusivity of the gelled
7 system.

8

9 Table 2 below details the thermal performance of
10 example 5.

11

12 Example 6

13

14 A second gelled fluid insulating system containing
15 76.5g of water, 8.5g of polyvinyl alcohol, 10g of
16 sunflower oil and 5g of cenospheres was similarly
17 made up, following the method of example 1.

18

19 0.5g of SbQ and 1g of acid (HCl 10%) was then added.

20

21 After a period of time, typically between one and
22 twenty four hours, the mixture sets as a solid
23 jelly-like material by undergoing the equivalent
24 aldol condensation reaction detailed above.

25

26 Some properties of this gel are set out in table 2,
27 below.

28

29 Example 7

30

31 A third all oil system was prepared. 16g of
32 cenospheres were stirred into a container holding

1 84g of kerosene. To this mixture 1g Clearwater HGA
2 70 (an orthophosphate ester) was added (although
3 between 0.3 and 1.5% by weight is suitable). The
4 mixture was gelled by the addition of 1g of
5 Clearwater HGA 55S (a ferric salt). Alternatively
6 ferric sulphate may be added at between 0.25 to 2.0
7 moles per mole of phosphate ester. The fluid was
8 left to gel for a period of 24 hours. In practice
9 however a gel formed typically between 2-5 minutes
10 from adding the ferric source.

11

12 Some of the properties of this gel are set out in
13 table 2 below which also shows a range of gelled
14 fluid insulating systems with different mixes of
15 oil, water and cenospheres.

16

17 Example 8

18

19 A fourth gelled fluid insulating system containing
20 10g of water, 1g of polyvinyl alcohol, 45g of
21 sunflower oil and 45g of cenospheres was similarly
22 made up, following the method of example 1.

23

24 0.05g of SbQ and 1g of acid (HCl 10%) was then
25 added.

26

27 After a period of time, typically between one and
28 twenty four hours, the mixture sets as a solid
29 jelly-like material by undergoing the equivalent
30 aldol condensation reaction detailed above.

31

1 Some properties of this gel are also set out in
 2 table 2, below.

3

4 In general the relative proportions of components in
 5 the gelled fluid insulating medium were determined
 6 using considerations of cost, ease of shipping to
 7 manufacturing location and desired performance
 8 characteristics.

9

10 Of particular interest is a measure of the rate of
 11 cool down known as diffusivity, this is described
 12 as:

13

14 Diffusivity = Conductivity (W/mK) / [Specific heat
 15 capacity(J/kg/K) x Density kg/m³]

16

17 The diffusivity measurements are given in table 2
 18 below.

19

Gel	Ratio of Components				Conduct- ivity ^[3] W/mK	Specific Heat ^[2] J/kgK	Density ^[3] kg/m ³	Diffus- ivity m ² /s (x 10 ⁻⁶)
	Oil ^[4]	Water	Other	Cenos- pheres				
5	45	18	2	PVA + 0.125 SbQ + 1 acid	35	0.22	1870	908
6	10	76.5	8.5	PVA + 0.5 SbQ + 1 acid	5	0.44	3790	982
7	84 ^[4]	0	1 C'HGA 70 (phosphate ester)	16	0.14	1740	863	0.093
8	45	10	1 C'HGA 55S (ferric salt)	45	0.17	1480	901	0.127

20 Table 2

21

1 Notes:

2 [1] Samples based on sunflower oil.
3 [2] Estimated from available data for constituents.
4 [3] Conductivity was measured using a non steady
5 state probe, ASTM method D5930-01
6 [4] Oil based gel using paraffinic oil.

7

8 Abbreviations

9

10 PVA - Polyvinylalcohol
11 SbQ - 4-(4-formylphenylethenyl)-1-methylpyridinium
12 methosulphonate
13 OPE - Orthophosphate ester
14 C'HGA 70 - Clearwater HGA 70 (phosphate ester)
15 C'HGA 55S - Clearwater HGA 55S (ferric salt)

16

17 The gelled fluid insulating media thermal
18 conductivities and diffusivities (a measure of the
19 rate of cool down) are comparable to those of
20 existing syntactic materials, which can go down to
21 $0.12W/mK$ and $0.12 \times 10^{-6} m^2/s$ respectively. While
22 low conductivity is required to provide the steady
23 state thermal performance on the flowing system, low
24 diffusivity is also desirable to maintain long cool-
25 down times.

26

27 In use, the pipeline bundles are made up on the
28 surface as is conventional in the art and an
29 oil/water/additive mixtures for example, those
30 detailed in examples 1-4 above, are then added to
31 the pipe-in-pipe annular space between the inner

1 pipes and the carrier pipe. The bundles are then
2 installed in the conventional manner.

3

4 The mixture has a sufficiently low viscosity to
5 enable it to be pumped into the pipe-in-pipe bundle
6 annular space where a reaction can take place which
7 results in the mixture forming into a gel as defined
8 in the Larousse Dictionary of Science and Technology
9 1995 page 470, that is a substance with properties
10 intermediate between the liquid and the solid
11 states.

12

13 The resulting gelled material is a jelly-like
14 substance and so can transmit the hydrostatic
15 pressure upon the external tubular or 'carrier' to
16 the inner tubulars. A further benefit of certain
17 embodiments of the present invention in using such
18 gelled fluid insulating media in pipe-in-pipe
19 systems is therefore that the external carrier pipe
20 does not need to be rated to hydrostatic pressure
21 experienced at depth since the gelled fluid
22 insulating media transfers the hydrostatic pressure
23 onto the inner tubulars.

24

25 A further consequence of certain embodiments of the
26 invention transmitting pressure is that they
27 maintain their integrity and insulating properties
28 unlike some prior art systems which can collapse and
29 lose their insulating properties at higher pressure.
30 Thus embodiments of the present invention do not
31 suffer the same depth limitations as syntactic foams

1 (although they will deform and recover at higher
2 stress).

3

4 The formation of a gel acts to prevent loss of heat
5 through convection. An advantage of certain
6 embodiments of the present invention is that the gel
7 possesses low conductivity, thereby providing
8 suitable insulating properties for deep water
9 applications.

10

11 Viscosity

12

13 An important advantage of certain embodiments of the
14 present invention is that the gelling material may
15 be poured into the annulus of the pipeline bundle
16 during set up but, once set into a gel, is of
17 "jelly-like" viscosity such that it cannot be
18 poured. This obviates the need for pressure-
19 balancing systems in particularly preferred
20 embodiments of the invention and also enables the
21 gel to transfer the hydrostatic pressure from the
22 sea to the inner pipelines in certain embodiments of
23 the invention. The outer pipelines can therefore be
24 made from cheaper, less robust, materials such as
25 thin steel or plastic.

26

27 The viscosity of various embodiments of the present
28 invention were determined as a function of gellant
29 addition using a dropped ball method based on a
30 modification of ASTM D1343-96(2000). Viscosity was
31 determined by measuring the rate at which a
32 stainless steel ball falls a predetermined distance

1 and applying this figure to a Stokes law
2 calculation.

3

4 Experimental Procedure

5

6 A stainless steel ball of diameter 12mm was weighed
7 and its density determined. A number of all-oil gel
8 formulations (equivalent to examples 1-4, 7 above)
9 in accordance with the present invention were
10 prepared over a range of additive concentrations and
11 placed into calibrated vessels. Gelling chemicals
12 were simply added to Atofina base oil DF1 although
13 any hydrocarbon could be used. The gels were left to
14 stand for a period of five days to ensure that the
15 gel had reached maximum strength. The stainless
16 steel ball was placed carefully on the surface of
17 the gel in the middle of the vessel. The ball's rate
18 of fall through the gel was determined by measuring
19 either the time it took the base of the ball to pass
20 between two calibrated points or the time it took
21 for the ball to pass from the base to the top of the
22 ball at one calibrated point. A number of readings
23 were taken and the average used to calculate the
24 viscosity using stokes equation as follows:

25

$$26 \quad V = (2gr^2)(d_1 - d_2) / 9\mu$$

27

28 where

29 V = velocity of fall (cm sec^{-1}),

30 g = acceleration of gravity (cm sec^{-2}), 980 cm sec^{-2}

31 r = "equivalent" radius of particle (cm),

32 d_1 = density of particle (g cm^{-3}),

1 d₂ = density of medium (g cm⁻³), and
 2 μ = viscosity of medium (dyne sec cm⁻²).

3

4 This can be rearranged to give
 5

6 $\mu = (2gr^2)(d_1-d_2)/90V$ as Pascal seconds (Pa.S)

7

8 The Results are displayed in the tables below and in
 9 Fig. 1.

10

radius of ball	0.6 cm
mass of ball	8.4 g
Volume of ball	0.904779 cm ³
density of ball	9.284038 g/cm ³
density of gel	0.79 g/cm ³
Density diff	8.494038 g/cm ³
Viscosity coefficient	66.59326

11

12

13

Additive concentration percent v/v		V sec/cm	Viscosity Pa S
HGA 55s	HGA 70		
0.5	0.5	2.26	150.5008
1	1	89	5926.8
1.5	1.5	913	60799.65
2	2	3404	226683.5

14

1 Viscosities in excess of 1000 Pa.S can be achieved
2 with additive concentrations in excess of 0.75
3 percent.

4

5 When this test was repeated using SbQ based oil
6 water gels (as with examples 5, 6 and 8 above) the
7 ball failed to penetrate the gel after a period of
8 20 hours indicating a viscosity in excess of
9 5,000,000 Pa.S had been attained.

10

11 **Determination of Gel Thermal Properties**

12

13 The thermal properties of the gels disclosed in
14 examples 1-4 and 7, that is the all-oil systems, was
15 studied. The quantities of the phosphate
16 ester/ferric salt etc. utilised do not significantly
17 affect the thermal conductivity and so were not
18 considered in these thermal conductivity
19 experiments. Rather, the thermal conductivity is a
20 function of the base oil, the proportion of
21 microspheres and the presence and concentration any
22 wax.

23

24 **Thermal conductivity measurements**

25

26 Thermal conductivity measurements were carried out
27 by means of a transient line source technique based
28 on ASTM method D 5930-01 calibrated using water and
29 olive oil materials with known thermal
30 conductivities. The calibration curve is shown in
31 Fig. 2 and produces a formula of

32

1 y = 2.7135x + 0.0002
2
3 that is:
4
5 Conductivity = 2.7135 x (Reading) + 0.0002
6
7 Measurements of thermal conductivity for the various
8 gels were then conducted. Conductivities were
9 determined for each measurement. The highest and
10 lowest values measured were discarded and an average
11 was taken.

12

13 Results

14

15 Sample 1 containing 5 percent microspheres - 7.5g in
16 150 ml oil gelled

17

Measurement ref	reading	conductivity value
DG0751	0.037861	0.108868754
DG0752	0.038073	0.109502994
DG0753	0.044272	0.128048542
DG0754	0.040853	0.11781992
DG0755	0.039689	0.114337581
DG0756	0.03741	0.107519497
DG0757	0.041316	0.119205077
DG0758	0.039945	0.115103457

18 Table 3

19

20 Average conductivity 0.114 W/m K

21

1 Sample 2 containing 20g microspheres in 60 ml gelled
 2 oil
 3

Measurement ref	reading	conductivity value
DG HS 01	0.02989	0.085021913
DG HS 02	0.03172	0.090496724
DG HS 03	0.032527	0.092911026
DG HS 04	0.028249	0.080112533
DG HS 05	0.028462	0.080749765
DG HS 06	0.028684	0.081413923

4 Table 4

5

6 Average conductivity 0.0807 W/m K

7

8 Sample 3 contains no microspheres but 30 g wax
 9 (Astorwax in 150 ml oil)

10

Measurement ref	reading	conductivity value
DG PC 01	0.046241	0.1339392
DG PC 02	0.05535	0.161190595
DG PC 03	0.050327	0.146163286
DG PC 04	0.050697	0.147270215
DG PC 05	0.049223	0.142860449

11 Table 5

12

13 Average Conductivity 0.1454W/m K

14

15 Sample 4 10g microspheres in 150 ml DF1 6.66 percent
 16 microspheres

17

Test no	measured	conductivity
DG 066 24304 1	0.034664	0.09426076
DG 066 24304 2	0.037873	0.10296839
DG 066 24304 3	0.03969	0.10789882
DG 066 24304 4	0.039727	0.10799921
DG 066 24304 5	0.038178	0.103796
DG 066 24304 6	0.03909	0.10627072
DG 066 24304 7	0.038178	0.103796
		0.7269899

1 Table 6

2

3 Average conductivity 0.104 W/m K

4

5 7.5 g microspheres in 150 ml 5 percent microspheres

6

7

8

9

10

11

12

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15

16

1

Test no	measured	conductivity
DG 05		
24304 1	0.041077	0.11166244
DG 05		
24304 2	0.040354	0.10970058
DG 05		
24304 3	0.043796	0.11904045
DG 05		
24304 4	0.038849	0.10561676
DG 05		
24304 5	0.039104	0.1063087
DG 05		
24304 6	0.040868	0.11109532
		0.66342425

2 Table 7

3

4 Average conductivity 0.111 W/m K

5

6 Fig. 3 plots all of the thermal conductivity
 7 measurements as a function of w/w percent sphere
 8 content. Fig. 3 shows a poor scatter at low levels
 9 of sphere content, however there is a linear
 10 relationship with a measurement of 0.12 W/mK. The
 11 addition of spheres does not contribute
 12 significantly to reducing the thermal conductivity
 13 of gel although they do lower the density of the gel
 14 and thereby improve its buoyancy. Table 8 details
 15 conductivity, specific heat capacity (C_p), density
 16 and diffusivity.

17

18

1

Sample	Conductivity K	Cp J / kg K	Density kg /m ³	Diffusivity x 10 ⁻⁸ m ² /s
DF 1 gel	0.12	2089	790	6.575
Gel PC AstorWax	0.137	2524	820	6.619
Gel 5% spheres	0.112	1881	728	8.18

2 Table 8

3

4 Fig. 4 plots the specific heat capacities for DF1
 5 liquid and DF1 gel and also DF1 gel containing 30g
 6 of two different waxes Flowax 210B - Gel A1 and
 7 Astorwax F07745B Gel B2.

8

9 The process of forming a gel with DF1 base oil has
 10 no effect on the Cp values.

11

12 Adding wax can however have a remarkable effect in
 13 particular with the Astorwax F07745B which is a high
 14 temperature branched chain wax with a melting around
 15 70°C. Here a phase transition is measured at
 16 approximately 52°C after which Cp values continue to
 17 climb. The phase change point is shifted and Cp
 18 levels continue to climb well above the levels found
 19 for DF1 gel on its own. Not all waxes work as well
 20 - Gel A1 containing Flowax 210B has a much different
 21 Cp profile with specific heat levels lower than the
 22 DF1 gel - this wax has a lower melting point than
 23 the Astorwax F07745 and it may be that a phase
 24 change has not occurred.

1 These two waxes tested have very different
2 structures. The Flowax 210B has a linear
3 conformation whereas the Astorwax F7745B is a
4 blended highly branched chain material. Thus highly
5 branched chain material are preferred.

6

7 Adding wax has two significant benefits:

8

9 It raises the Cp value significantly and at lower
10 temperatures the phase change of the wax
11 precipitating out to wax crystallites provides a
12 secondary mechanism to prevent convection to support
13 the gel structure.

14

15 The Cp behaviour with the F7745B is particularly
16 significant since it appears to "recruit" the base
17 oil hydrocarbon into the gelling process, rather
18 than act solely as a phase change material.

19

20 A further advantage of certain embodiments of the
21 present invention is the high thermal mass and low
22 diffusivity of the gel which increases cool-down
23 times and gives operational flexibility for long
24 tie-backs and remote deep water production systems.

25

26 A further benefit of certain embodiments of the
27 present invention is that the thermal performance of
28 the gels, including conductivity and heat capacity,
29 can be varied and thus suitably tailored for
30 individual systems by varying the relative
31 components of oil, water and cenospheres. Thus
32 different compositions of the gels are used

1 depending on the specific nature of the fluids being
2 transported, the pipeline arrangement, the subsea
3 environment and other factors.

4

5 For instance, examples 3 and 6 have a high specific
6 heat capacity making them suitable for applications
7 where a long cool down performance is required.

8 Example 2 and 8 by contrast have a much lower
9 thermal conductivity and so it would be particularly
10 suited to ensure high pipeline fluid arrival
11 temperatures thereby easing fluid processing.

12 Example 7 offers a balance between thermal
13 conductivity and good cool down performance although
14 it has a less favourable environmental profile.

15 Example 4 has a low thermal conductivity but also
16 exhibits very low density and could be used in riser
17 applications or as a deepwater buoyancy system.

18

19 Therefore certain embodiments of the present
20 invention can be used solely as a buoyancy aid
21 rather than for insulation. Indeed the density of
22 the gel can be varied between the bottom and the top
23 of a single conduit - the top of the conduit can
24 have a gel with a higher proportion of spheres and
25 therefore lower density than the bottom of the
26 conduit. The riser will therefore automatically
27 right itself when immersed in water.

28

29 A further benefit of certain embodiments of the
30 invention is that different formulations of gel can
31 be used in the same pipeline. For instance at the
32 pipeline closest to the subsea wellhead hydrocarbons

1 will be at their highest temperature and so a gel
2 formulation with a low conductivity (such as example
3 2) is preferred to minimise heat loss. At the other
4 end of the pipeline, fluids are at their coldest and
5 most prone to wax deposition and so the gel
6 formulation with an enhanced specific heat capacity
7 (such as example 3) is preferred to improve the cool
8 down performance and thereby minimise the incidence
9 of wax or hydrate formation.

10

11 A further benefit of certain embodiments of the
12 invention is that a gel can be made containing high
13 concentrations of pressure resistant microspheres
14 with the interstices between spheres filled with oil
15 as in example 4. Such a material can be usefully
16 employed as a means of deep water buoyancy.

17 A further benefit of certain embodiments of the
18 present invention is the low toxicity and generally
19 non-hazardous materials which are used which
20 facilitates handling, transportation and disposal.

21

22 Moreover, the cost of certain embodiments of the
23 present invention is less than previous syntactic
24 'wet' coatings or silica based pipe-in-pipe systems,
25 they can be made on site and do not require
26 expensive storage or mixing facilities and a
27 pressure-rated outer carrier pipe is not required.

28

29 The thermal properties can be improved further by
30 selecting materials that undergo a change in phase
31 (such as going from a liquid to a solid) on cooling.
32 This change in phase will result in the release of

1 heat thereby extending the time it takes for the
2 pipeline contents to cool down. Gels can be made
3 with such phase change materials by melting the
4 material to render it in its liquid form and adding
5 additives to this.

6

7 Other chemicals such as anti bacterial agents, for
8 example DowTM Antimicrobial 7287, Avecia Proxel XL2
9 or Rhodia Tolcide PS50D, or corrosion inhibitors for
10 example imidazoline, amine salts or phosphate esters
11 or oxygen or free radical scavengers such as
12 erthorbic acid or tertiary butyl hydroquinone can
13 also be added to this gelled fluid insulating
14 medium.

15

16 Improvements and modifications may be made without
17 departing from the scope of the invention.

18